# Fourier Transform Ion Cyclotron Resonance Studies of Lanthanide(III) Porphyrin-Phthalocyanine Heteroleptic Sandwich Complexes by Using Electrospray Ionization

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A number of neutral lanthanide(III) porphyrin-phthalocyanine heteroleptic sandwich complexes have been studied by using positive-ion electrospray ionization–Fourier transform ion cyclotron resonance mass spectrometry. The investigated compounds are represented as $Ln^{III}(TPP)(Pc)$, $Ln_2^{III}(TPP)(Pc)_2$, and $Ln_2^{III}(TPP)_2(Pc)$, where Ln = Sm, Eu, or Gd, TPP is 5,10,15,20-tetraphenylporphyrinate, and Pc is phthalocyaninate. In all cases, intense signals corresponding to the singly charged molecular radical cations are observed. The formation of these molecular radical cations in electrospray ionization is attributed to electrochemical oxidation at the electrospray needle. Multiply charged molecular ions up to +5 are also observed. They are tentatively assigned to be formed from successive oxidation of the ligand(s). Apart from the molecular weight information, tandem mass spectrometry offers additional structural information on these complexes. From the fragmentation pattern of the europium complexes under collision-induced dissociation conditions, the configurations of the triple-decker complexes are assigned mass spectrometrically to be (TPP)Eu(Pc)Eu(Pc) and (TPP)Eu(Pc)Eu(TPP). In comparison with the previous spectroscopic findings that the positive "hole" is localized in the ligands of the complexes, there is evidence to suggest that intramolecular charge transfer or hole delocalization does occur within the macrocycles or between the metal centers and the macrocycles before fragmentation. The occurrence of this charge-transfer process is tentatively attributed to the result of collisional activation.  *(J Am Soc Mass Spectrom 1997, 8, 161–169)*

Sandwich-type complexes of porphyrins and phthalocyanines have aroused increasing interest during recent years. These complexes have potential applications as prototype materials for visual displays [1], semiconductors [2–4], and gas sensors in pollution control [5]. The strong $\pi$-$\pi$ interaction between the macrocycles also enables these complexes to serve as models in studying the structure and spectroscopic properties of the "special pair" in the reaction center of photosynthetic bacteria [6–8]. Although the homoleptic complexes have been extensively investigated, examples of the heteroleptic analogs having mixed porphyrinato and phthalocyaninato ligands are rare [9]. For the neutral double-decker complexes of tervalent lanthanides Ln(Pc)(Por) (Pc = phthalocyaninate; Por = general porphyrinate), there exists a charge imbalance between the metal centers and the dianionic ligands. Structural and spectroscopic studies have shown that these complexes are in a nonprotonated, one-electron oxidized ligand form, $Ln^{III}(Pc^{\cdot -})(Por^{2-})$, in which the hole preferentially resides on the Pc macrocycle [10–12]. The only exception is the La complex LaH(Pc)(TPP), which contains a protonated macrocycle [11]. These sandwich compounds undergo up to four reversible one-electron transfers as revealed by cyclic voltammetry. The first oxidation and reduction processes both involve the macrocyclic ligands, whereas the metal center keeps its oxidation state as III, which is the most characteristic oxidation state of the lanthanides [13]. For the analogous triple-decker complexes $Ln_2(Pc)_x(Por)_{3-x}$ ($x$ = 1, 2), the two $Ln^{III}$ ions are sandwiched between the $Pc^{2-}$ and $Por^{2-}$ ligands, resulting in neutral complexes [9, 10, 14–16]. Oxidation of these metal sandwiches in which the metal cannot be oxidized (e.g., Gd, Eu) [17] is associated with the macrocycles. For the Ce(III) derivatives, the metal centers may also be involved in the redox processes [10].

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Structural characterization of these sandwich complexes by NMR and x-ray crystallography can provide insight into the symmetry of the molecules and the geometrical arrangement of atoms within the complexes [11, 15, 18–20]. These techniques, however, require a sample size of milligrams. Whereas molecular weight measurement by using mass spectrometric methods is often complicated by high molecular weight, involatility and thermal liability, the use of mass spectrometry to characterize these complexes has been limited to simple metalloporphyrins and metallophthalocyanines [21–26].

In this paper, we present experimental results for the analysis of a series of neutral heteroleptic lanthanide(III) porphyrin-phthalocyanine complexes by using electrospray ionization (ESI) mass spectrometry. ESI provides a fast, sensitive, and accurate method for molecular weight determination (for reviews, see refs 27–31). Because of the softness of the desorption–ionization process(es), little or no observable fragmentation of the sandwich complexes has been observed. Tandem mass spectrometry (MS/MS) studies of the desorbed ions provide important information on the structural arrangement of the porphyrin and phthalocyanine rings within the complexes. In addition, the observation of some unexpected fragment ions provides evidences to support the occurrence of charge-transfer processes under collision-induced dissociation (CID) conditions. Both intramolecular charge transfer within the molecule ions and intermolecular charge transfer between the molecule ions and the collision gas are possible. Their relative contributions to the observed spectra are discussed.

## Experimental

### *Instrumentation*

ESI mass spectra were acquired with a 4.7-T Fourier transform ion cyclotron resonance (FTICR) mass spectrometer (Bruker Instrument, Billerica, MA) equipped with an external ESI source with an Iris™ hexapole ion guide (Analytica, Bradford, CT).

Analyte solutions were introduced into the ESI source with a syringe pump at a flow rate of 1–3 $\mu$L/min. The capillary entrance was normally held at a potential of −4.5 kV relative to the grounded needle. Nitrogen countercurrent drying gas was heated to 200°C and was introduced into the capillary region at a flow rate of 1–5 L/min. A sheath flow of nitrogen gas was introduced through the outer layer of the triply layered electrospray needle to stabilize and assist the spray.

Nozzle–skimmer (NS) dissociation experiments [32–34] were performed by raising the capillary exit lens (Figure 1) to +400 V. For sustained off-resonance irradiation collision-induced dissociation (SORI-CID) experiments [35, 36], the singly charged molecular ions were first mass-selected by preferentially exciting and ejecting other ions. Collision gas ($CO_2$) was pulsed into the trap cell. The analyzer pressure increased from $10^{-9}$ to $10^{-7}$ torr. After a pump-down delay of 0.5 s,

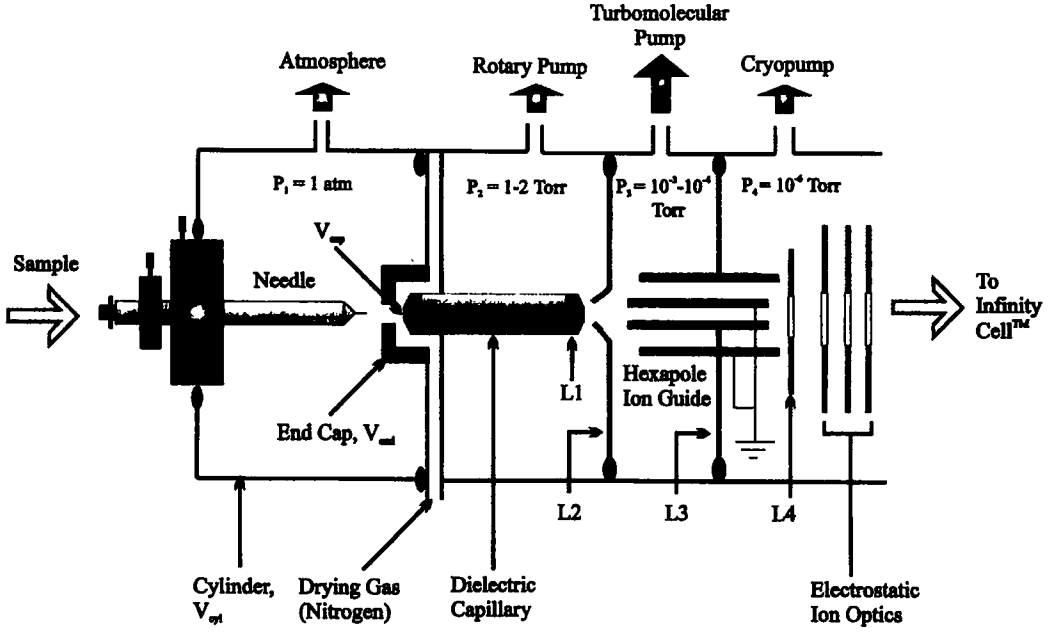



**Figure 1.** A schematic of the modified ESI source. Typical potentials for positive-ion ESI: needle, 0 V; $V_{cyl}$, −3600 V; $V_{end}$, −4200 V; $V_{cap}$, −4800 V; L1, +100 V (non-CID and SORI-CID conditions) or +400 V (NS dissociation conditions); L2, + (2–5) V; L3, + (40–50) V; L4, pulsed between + (10–20) and −(5–10) V.

the molecule ions were activated by using a 2.4-ms, 105-$V_{peak\text{-}to\text{-}peak}$ electric field pulse with a frequency offset of 1 kHz lower than the corresponding ion cyclotron frequency of the molecular ions. A delay of 2 s was used after the activation to allow metastable fragmentation of the activated ions. The molecule ions together with the resulting fragment ions were then excited by a chirp and detected.

All mass spectra were acquired in broadband mode (unless otherwise stated) with time domain signals of 128K data points. Thirty scans were summed to improve signal-to-noise ratio. All spectra were apodized with a Gaussian function and zero-filled once prior to Fourier transformation. The instrument was normally calibrated by using bovine insulin (Sigma, Chemical Co., St. Louis, MO) in a 49:49:2 (percent volume) water:methanol:acetic acid solution. In all experiments, trapping potentials of 1 V were used.

### *Sample Preparation*

In general, neutral lanthanide(III) porphyrin-phthalocyanine complexes were prepared by treating dilithium phthalocyaninate [$Li_2(Pc)$] with $Ln^{III}(acac)(TPP)$ (Ln = Sm, Eu or Gd; acac = acetylacetonate; TPP = 5,10,15,20-tetraphenylporphyrinate) prepared in situ from $Ln(acac)_3.nH_2O$ and $(TPP)H_2$ in 1,2,4-trichlorobenzene. Triple-decker complexes were formed along with a small amount of double-decker complexes. The products were separated chromatographically and further purified by recrystallization from a 2:1 mixture of $CH_2Cl_2/CH_3OH$ [9]. For mass spectrometric measurements, ~ 0.1 mg of a purified lanthanide complex was dissolved in 1 mL of high-performance liquid chromatography grade dichloromethane.

## Results and Discussion

The heteroleptic lanthanide(III) porphyrin-phthalocyanine complexes examined in this study are shown in Figure 2. For triple-decker sandwich complexes, there are two possible configurations, that is, symmetric and asymmetric, as shown in Figure 2b and c. By using MS/MS, the exact configuration of these triple-decker complexes can be obtained (see following text).

### *Electrospray Ionization Mass Spectra*

The positive-ion ESI mass spectra of the heteroleptic double-decker complexes of Sm, Eu, and Gd exhibit strong signals corresponding to the singly charged molecular ions. The molecular masses are summarized in Table 1. Figure 3 displays a typical ESI mass spectrum of Eu(TPP)(Pc). Comparing the observed isotopic distribution of $[Eu(TPP)(Pc)]^+$ with the simulated spectra based on the diradical ion $M:^+$ and the protonated radical ion $[M + H]^{\cdot +}$ (Figure 4), it is believed that both types of molecular ions were present. However, contributions from other protonated and/or deprotonated species cannot be ruled out.

The mechanism of ion formation in ESI was previously postulated by Kebarle and co-workers [37] by using an electrophoretic model. The high electric field at the needle tip leads to a spatial separation of the positive and negative ions in the sample solution. In the positive-ion mode, the Coulombic repulsion between positive ions at the needle tip destabilizes the liquid surface and results in the emission of positively charged droplets. To maintain the neutrality of the solution, oxidation reaction(s) must occur within the solution which ultimately leads to a flow of electrons to ground. Analysis of neutral molecules by using ESI recently was reported [38–43]. Dupont et al. [41] showed that neutral compounds with redox potentials between −0.8 and +1.0 V versus standard calomel electrode (SCE) in pure dichloromethane could be analyzed by electrospray ionization–mass spectrometry (ESI-MS) without any previous electrolysis to their ionized forms. These molecules were believed to be ionized to their molecular radical cations by on-line electrochemical oxidation at the electrospray (ES) source, in which the source behaves like an electrolysis cell [38, 39, 42]. The redox potentials corresponding to a one-electron oxidation of Eu(TPP)(Pc) and Gd(TPP)(Pc) were previously reported by Chebach et

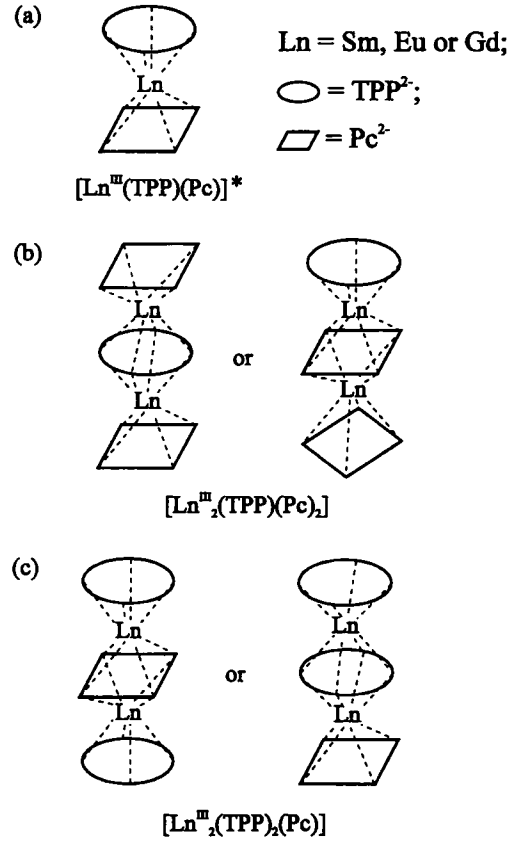



**Figure 2.** Structures of the heteroleptic sandwich complexes (a) $Ln^{III}(TPP)(Pc)$, (b) $Ln^{III}_2(TPP)(Pc)_2$, and (c) $Ln^{III}_2(TPP)_2(Pc)$. The asterisk (*) denotes that in the neutral double-decker complexes, one of the macrocycles exists as $TPP^{\cdot -}/Pc^{\cdot -}$ or $TPPH^-/PcH^-$ to give an overall charge of zero.

**Table 1.** Summary of the molecular masses of the heteroleptic lanthanide(III) sandwich complexes

| Compound | Molecular formula | Mass (*m/z*) | | | |
|---|---|---|---|---|---|
| | | Proposed ionic species | Calculated value[a] | Measured value | Error (u) |
| Sm(TPP)(Pc) | $C_{76}H_{44}N_{12}Sm$ | $M^{\cdot+}$, $[M+H]^{\cdot+}$ | 1278.301 | 1278.289 | 0.012 |
| Eu(TPP)(Pc) | $C_{76}H_{44}N_{12}Eu$ | $M^{\cdot+}$, $[M+H]^{\cdot+}$ | 1277.306 | 1277.314 | 0.008 |
| Gd(TPP)(Pc) | $C_{76}H_{44}N_{12}Gd$ | $M^{\cdot+}$, $[M+H]^{\cdot+}$ | 1282.301 | 1282.306 | 0.005 |
| $Sm_2(TPP)(Pc)_2$ | $C_{108}H_{60}N_{20}Sm_2$ | $M^{\cdot+}$ | 1938.361 | 1938.435 | 0.074 |
| $Eu_2(TPP)(Pc)_2$ | $C_{108}H_{60}N_{20}Eu_2$ | $M^{\cdot+}$ | 1941.374 | 1941.396 | 0.022 |
| $Gd_2(TPP)(Pc)_2$ | $C_{108}H_{60}N_{20}Gd_2$ | $M^{\cdot+}$ | 1952.387 | 1952.262 | 0.125 |
| $Sm_2(TPP)_2(Pc)$ | $C_{120}H_{72}N_{16}Sm_2$ | $M^{\cdot+}$ | 2038.438 | 2038.041 | 0.397 |
| $Eu_2(TPP)_2(Pc)$ | $C_{120}H_{72}N_{16}Eu_2$ | $M^{\cdot+}$ | 2041.451 | 2041.429 | 0.022 |
| $Gd_2(TPP)_2(Pc)$ | $C_{120}H_{72}N_{16}Gd_2$ | $M^{\cdot+}$ | 2052.464 | 2052.208 | 0.256 |

[a]Mass corresponding to the most abundant isotopic peak of the nonprotonated species.

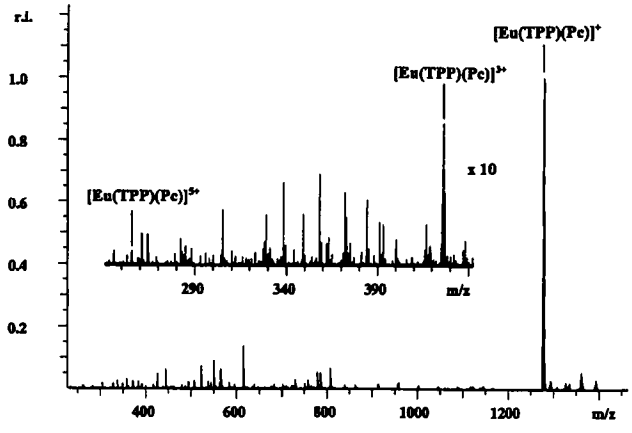



**Figure 3.** A typical positive-ion ESI mass spectrum of Eu(TPP)(Pc) (L1 = 100 V).

al. [11] as 0.535 and 0.555 V versus SCE, respectively. Whereas the one-electron oxidation potentials for these sandwich complexes are well within the limits [41] for on-line electrochemical oxidation at the ES source, the ion formation of these sandwich complexes, in the present study, was tentatively attributed to the electrochemical oxidation at the metal–solution interface in the ES needle. The neutral double-decker complexes were postulated to exist in both the nonprotonated one-electron oxidized ligand form $(TPP^{2-})Ln^{3+}(Pc^{\cdot-})$ and/or $(TPP^{\cdot-})Ln^{3+}(Pc^{2-})$ and the protonated form $(TPP^{2-})Ln^{3+}(H^+)(Pc^{2-})$; they lose an electron to give the diradical cations $[(TPP^{\cdot-})Ln^{3+}(Pc^{\cdot-})]^+$ and the protonated monoradical cations $[(TPP^{2-})Ln^{3+}(H^+)(Pc^{\cdot-})]^+$ and/or $[(TPP^{\cdot-})Ln^{3+}(H^+)(Pc^{2-})]^+$. This accounts for the distorted isotopic distribution of the observed singly charged molecular ions. In addition to the singly charged species, signals corresponding to the multiply charged molecular ions can also be observed, as shown in Figure 5. They are tentatively assigned to be formed from successive oxidation of the ligand(s) [44].

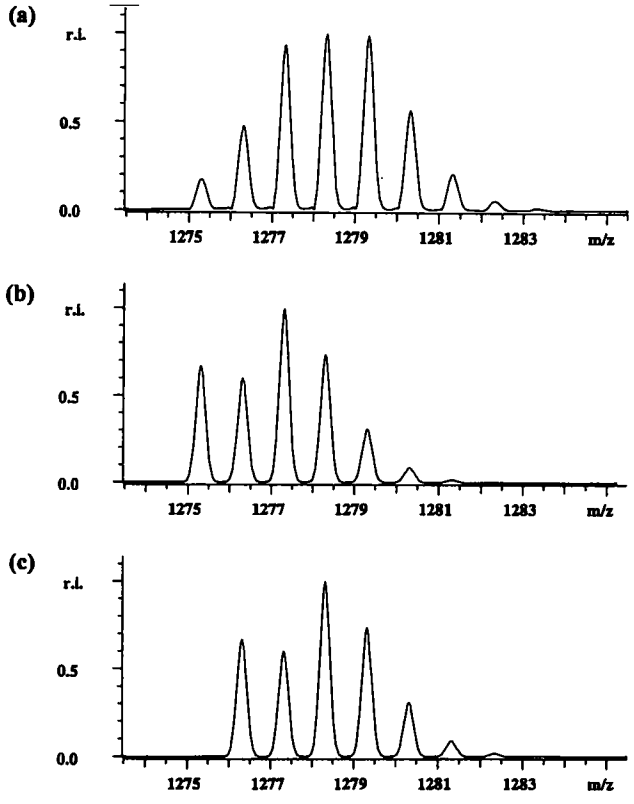



**Figure 4.** A comparison of the observed isotopic distribution of (a) $[Eu(TPP)(Pc)]^+$ and the simulated spectra based on (b) the diradical ion and (c) the protonated radical ion.

For the heteroleptic triple-decker complexes of Sm, Eu, and Gd, singly charged molecular ions formed the predominant species under ESI conditions. The molecular masses are summarized in Table 1. Figure 6 shows a typical positive-ion ESI mass spectrum of the $Eu_2(TPP)(Pc)_2$. The observed isotopic distribution of $[Eu_2(TPP)(Pc)_2]^+$ is in good agreement with the simulated spectrum of the radical monocation ($M^{\cdot+}$) (Figure 7). This implies that the neutral heteroleptic triple-decker complexes exist only in one form, that is, as

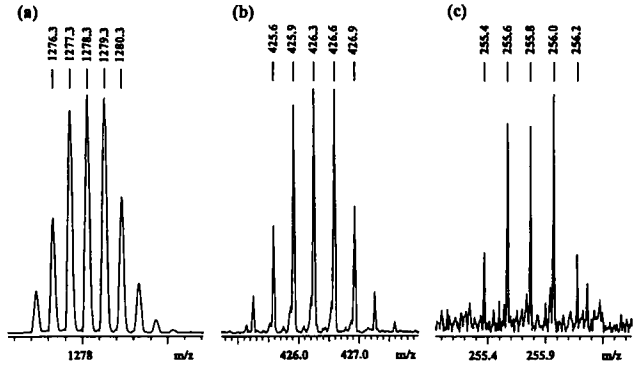



**Figure 5.** Partial ESI mass spectra of Eu(TPP)(Pc) showing the expanded region of several multiply charged ions: (a) $[Eu(TPP)(Pc)]^+$, (b) $[Eu(TPP)(Pc)]^{3+}$, and (c) $[Eu(TPP)(Pc)]^{5+}$.

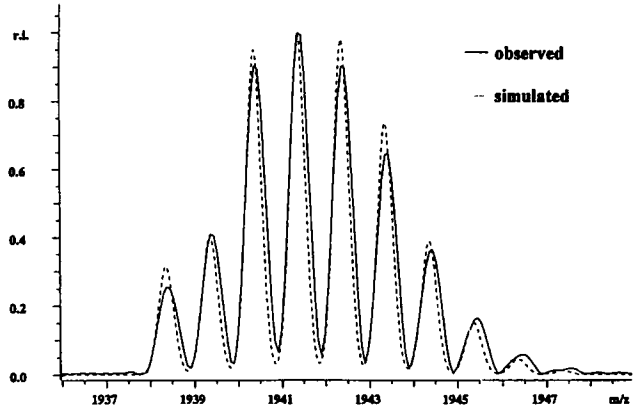



**Figure 7.** A comparison of the observed isotopic distribution of $[Eu_2(TPP)(Pc)_2]^+$ and the simulated spectrum of the radical monocation.

$(Eu^{3+})_2(TPP^{2-})(Pc^{2-})_2$ for $Eu_2(TPP)(Pc)_2$. One-electron oxidation of the neutral complexes leads solely to singly charged radical monocations. Similar to the double-decker complexes, multiply charged ions arising from successive oxidation of the ligand(s) of the triple-decker complexes can also be observed (Figure 8). It is interesting to point out that even-charged species were not detected with significant abundance in either double- and triple-decker complexes.

## *Collision-Induced Dissociation Mass Spectra*

In an attempt to determine the configurations of the triple-decker heteroleptic sandwich complexes, both non-mass-selective (NS) dissociation and mass-selected SORI-CID experiments were performed on the europium complexes.

Figure 9a and b shows the mass spectra of $Eu_2(TPP)(Pc)_2$ obtained under NS dissociation and SORI-CID conditions, respectively. The spectral information is summarized in Table 2. In the NS dissociation mass spectrum, the singly charged molecular ions remained predominant. This is consistent with the high stability of these heteroleptic complexes. Fragment signals corresponding to the breakdown of the triple-decker structure can be clearly identified. Characteristic ions such as $[(TPP)Eu(Pc)]^{n+}$ and $[(Pc)Eu(Pc)]^{n+}$ (where $n$ = 1, 3, or 5) can be used to support the asymmetric configuration for $Eu_2(TPP)(Pc)_2$. Nevertheless, owing to the nature of NS dissociation and the fact that some of these characteristic ions were already observed even under non-CID conditions, it is difficult to confirm whether these ions originated from dissociation of the molecular ions or pre-existed in solution.

To verify the results, mass-selected SORI-CID experiments were performed. Special attention was paid to ensure good isolation of the singly charged molecular ions $[Eu_2(TPP)(Pc)_2]^+$ prior to CID experiments. SORI was employed to promote fragmentation. In all experiments, a frequency downshift of 1 kHz was used. Substantial fragment ions were generated by using this method as shown in Figure 9b. Of particular interest is the formation of $[(TPP)Eu(Pc)]^+$ and $[Eu(Pc)_2]^+$ ions. This triple-decker complex is there-

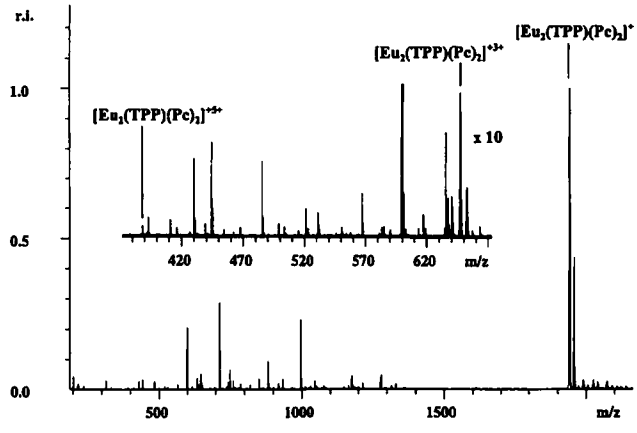



**Figure 6.** A typical positive-ion ESI mass spectrum of $Eu_2(TPP)(Pc)_2$ (L1 = 100 V).

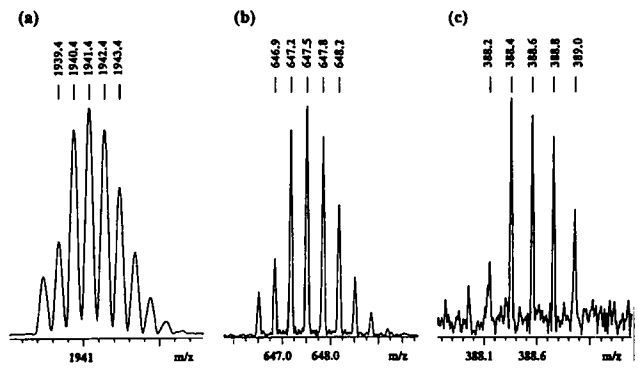



**Figure 8.** Partial ESI mass spectra of $Eu_2(TPP)(Pc)_2$ showing the expanded region of several multiply charged ions: (a) $[Eu_2(TPP)(Pc)_2]^+$, (b) $[Eu_2(TPP)(Pc)_2]^{3+}$, and (c) $[Eu_2(TPP)(Pc)_2]^{5+}$.

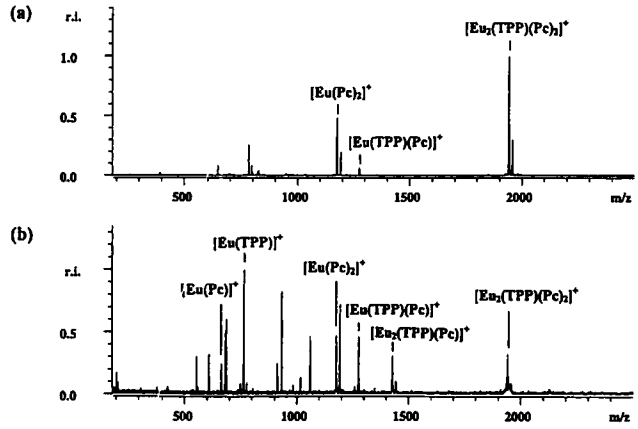



**Figure 9.** (a) NS dissociation (L1 = 400 V) and (b) SORI-CID (L1 = 100 V) mass spectrum of $Eu_2(TPP)(Pc)_2$.

fore structurally assigned to be asymmetric, that is, (TPP)Eu(Pc)Eu(Pc).

Figure 10a and b shows the mass spectra of $Eu_2(TPP)_2(Pc)$ obtained under NS dissociation and SORI-CID conditions, respectively. The spectral information is summarized in Table 3. Suppose $Eu_2(TPP)_2(Pc)$ also takes an asymmetric configuration as $Eu_2(TPP)(Pc)_2$ does; two characteristic fragment ions $[(TPP)Eu(Pc)]^{n+}$ and $[(TPP)Eu(TPP)]^{n+}$ (where n is an integer) would be expected. However, it was found that only $[(TPP)Eu(Pc)]^+$ ions were observed. There was no signal corresponding to $[(TPP)Eu(TPP)]^{n+}$ ions under either NS dissociation or SORI-CID conditions. This triple decker complex is therefore believed to adopt a symmetric configuration (TPP)Eu(Pc)Eu(TPP). The assignment has been supported by $^1H$ NMR spectrometry [9]. Based on the symmetric configuration of $Eu_2(TPP)_2(Pc)$, the fragment ions $[Eu(Pc)]^+$ are proposed to be formed from the daughter ions $[(TPP)Eu(Pc)]^+$ rather than directly from the parent ions, in which simultaneous cleavage of two bonds is required which is believed to be unfavorable.

## *Charge-Transfer Processes*

The observation of characteristic fragment ions provides eminent support for the assignment of the configurations of the heteroleptic triple-decker complexes. It is however extremely important to evaluate the possibility of fragmentation in terms of electronic arrangement.

Considering the fragmentation pattern of $[Eu_2(TPP)(Pc)_2]^+$, it would be impossible to account for the observation of some singly charged fragment ions, such as $[Eu(TPP)(Pc)]^+$ and $[Eu(Pc)_2]^+$, without assuming intramolecular charge transfer prior to fragmentation. To observe $[Eu(TPP)(Pc)]^+$, the ligands associated with this fragment ion must be oxidized to give an overall charge of $2^-$. In a typical low energy fragmentation, cleavage of a singly charged molecular ion usually leads to the formation of a singly charged fragment ion and a neutral fragment. To account for the loss of neutral fragment [Eu(Pc)], either the ligand (Pc) or the metal center (Eu) would have to be reduced to its $-3$ or $+2$ state, respectively. From the known stability of $Pc^{3-}$ [44, 45] and $Eu^{2+}$ [17, 46], both of these reduction processes are possible. The results obtained in the present study strongly suggest that intramolecular charge-transfer reactions occurred between the macrocyclic ligands or/and between the metal center(s) and the macrocyclic ligands. The fragmentation pathways for $Eu_2(TPP)(Pc)_2$ are summarized in Scheme Ia. Based on the same argument, the fragmentation pathways for $Eu_2(TPP)_2(Pc)$ are illustrated in Scheme Ib.

Although $CO_2$ has a relatively low tendency of reduction, the possibility of intermolecular charge transfer between the parent ions and the collision gas has also been evaluated. Considering $[Eu_2(TPP)(Pc)_2]^+$, further oxidation of this monocation would lead to doubly charged molecular ions, that is, $[Eu_2(TPP)(Pc)_2]^{2+}$. However, such doubly charged ions were not observed. This implies that either the inter-

**Table 2.** Summary of the fragment information of $Eu_2(TPP)(Pc)_2$

| Proposed ionic species | Calculated value[b] | Non-CID conditions[a] | | NS dissociation | | Mass-selected SORI-CID | |
|---|---|---|---|---|---|---|---|
| | | *m/z* | r.i.[c] | *m/z* | r.i.[c] | *m/z* | r.i.[c] |
| $[Eu_2(TPP)(Pc)_2]^+$ | 1941.4 | 1941.4 | 100.0 | 1941.4 | 100.0 | 1942.6 | 26.4 |
| $[Eu_2(TPP)(Pc)_2]^{2+}$ | 970.7 | 970.7 | 0.5 | 970.7 | 0.7 | — | — |
| $[Eu_2(TPP)(Pc)_2]^{3+}$ | 647.1 | 647.6 | 5.1 | 647.5 | 8.3 | — | — |
| $[Eu_2(TPP)(Pc)_2]^{5+}$ | 388.3 | 388.6 | 0.4 | 388.6 | 1.0 | — | — |
| $[Eu_2(TPP)(Pc)]^+$ | 1428.2 | — | — | 1428.2 | 0.6 | 1428.2 | 31.0 |
| $[Eu(TPP)(Pc)]^+$ | 1277.3 | 1277.3 | 3.5 | 1277.3 | 6.3 | 1277.3 | 46.4 |
| $[Eu(TPP)(Pc)]^{3+}$ | 425.8 | — | — | 425.9 | 0.2 | — | — |
| $[Eu(Pc)_2]^+$ | 1177.2 | 1177.2 | 3.9 | 1177.2 | 47.9 | 1177.2 | 47.1 |
| $[Eu(Pc)_2]^{3+}$ | 392.4 | 392.6 | 0.1 | 392.5 | 2.8 | — | — |
| $[Eu(TPP)]^+$ | 765.2 | — | — | 765.2 | 1.3 | 765.1 | 100.0 |
| $[Eu(Pc)]^+$ | 665.1 | — | — | 665.1 | 0.4 | 665.1 | 24.8 |

[a] Ionic species observed under non-CID conditions are listed for comparison.
[b] Mass corresponding to the most abundant isotopic peak.
[c] r.i. denotes relative intensity.

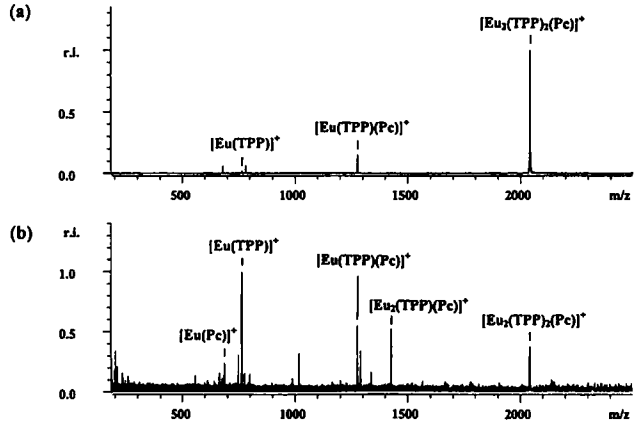
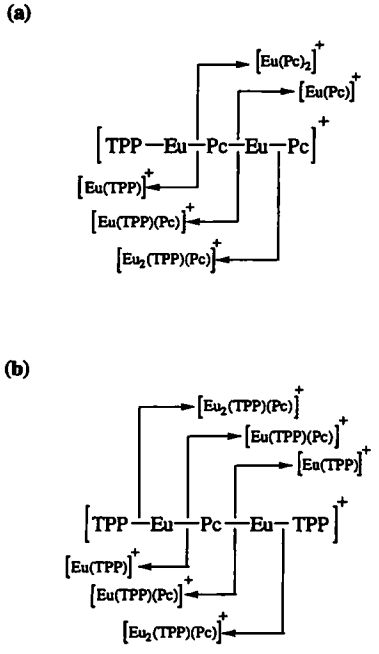



**Figure 10.** (a) NS dissociation (L1 = 400 V) and (b) SORI-CID (L1 = 100 V) mass spectrum of $Eu_2(TPP)_2(Pc)$.

molecular charge transfer did not occur or the doubly charged ions underwent prompt dissociation to form $[Eu(TPP)(Pc)]^+$ and $[Eu(Pc)]^+$ or $[Eu(Pc)_2]^+$ and $[Eu(TPP)]^+$. The latter dissociation process(es) follows the low energy pathway because of the repulsion between the two positively charged fragments. To test this hypothesis, mass-selected SORI-CID spectra of $[Eu(TPP)(Pc)]^+$ were obtained. Results are summarized in Table 4. Signals corresponding to the singly charged $[Eu(TPP)]^+$ and $[Eu(Pc)]^+$ can clearly be observed. If charge transfer does occur between the parent ions and $CO_2$, doubly charged $[Eu(TPP)(Pc)]^{2+}$ would result. Again, this ion was not observed. If this ion does occur and undergoes prompt dissociation to give $[Eu(TPP)]^+$ and $[Eu(Pc)]^+$ ions, other product ions such as $Pc^{\cdot+}$ and $TPP^{\cdot+}$ must also form. No signals corresponding to $Pc^{\cdot+}$ and $TPP^{\cdot+}$ ions were observed, however. Therefore, it is believed that intermolecular charge transfer does not contribute significantly in our cases. To account for the observed $[Eu(TPP)]^+$ and $[Eu(Pc)]^+$, intramolecular charge transfer within the complexes has to be assumed. This is in consistent with the low energy fragmentation pathways that involve the loss of neutral Pc: and TPP: moieties.

## Conclusion

Lanthanide(III) porphyrin-phthalocyanine sandwich complexes were mass-characterized by using ESI-FTICR. With the use of both NS dissociation and MS/MS techniques, the structure and electronic properties of the europium complexes were studied and reported. The synergy of the techniques enables us to establish two pieces of important information. First, mass spectrometry allows direct determination of the




**Scheme 1.** Proposed fragmentation pathways for (a) $Eu_2(TPP)(Pc)_2$ and (b) $Eu_2(TPP)_2(Pc)$.

**Table 3.** Summary of the fragment information of $Eu_2(TPP)_2(Pc)$

| Proposed ionic species | Calculated value[b] | Non-CID conditions[a] | | NS dissociation | | Mass-selected SORI-CID | |
|---|---|---|---|---|---|---|---|
| | | *m/z* | r.i.[c] | *m/z* | r.i.[c] | *m/z* | r.i.[c] |
| $[Eu_2(TPP)_2(Pc)]^+$ | 2041.5 | 2041.4 | 79.5 | 2041.3 | 92.9 | 2041.3 | 34.7 |
| $[Eu_2(TPP)_2(Pc)]^{2+}$ | 1020.7 | 1020.7 | 0.2 | 1020.8 | 0.8 | — | — |
| $[Eu_2(TPP)_2(Pc)]^{3+}$ | 680.5 | 680.9 | 5.4 | 680.9 | 6.0 | — | — |
| $[Eu_2(TPP)_2(Pc)]^{4+}$ | 510.4 | — | — | 510.6 | 0.1 | — | — |
| $[Eu_2(TPP)_2(Pc)]^{5+}$ | 408.3 | 408.6 | 0.5 | 408.6 | 0.7 | — | — |
| $[Eu_2(TPP)(Pc)]^+$ | 1428.2 | — | — | 1428.2 | 0.7 | 1428.2 | 52.6 |
| $[Eu(TPP)(Pc)]^+$ | 1277.3 | 1277.3 | 2.0 | 1277.3 | 11.5 | 1277.2 | 55.5 |
| $[Eu(TPP)(Pc)]^{2+}$ | 638.7 | — | — | 638.7 | 0.1 | — | — |
| $[Eu(TPP)(Pc)]^{3+}$ | 425.8 | — | — | 426.0 | 0.5 | — | — |
| $[Eu(TPP)]^+$ | 765.2 | — | — | 765.2 | 1.9 | 765.1 | 100.0 |
| $[Eu(Pc)]^+$ | 665.1 | — | — | 665.1 | 0.5 | 665.1 | 16.4 |

[a] Ionic species observed under non-CID conditions are listed for comparison.
[b] Mass corresponding to the most abundant isotopic peak.
[c] r.i. denotes relative intensity.

**Table 4.** Summary of the Fragment Information of Eu(TPP)(Pc)

| Proposed ionic species | Calculated value[b] | Non-CID conditions[a] | | NS dissociation | | Mass-selected SORI-CID | |
|---|---|---|---|---|---|---|---|
| | | *m/z* | r.i.[c] | *m/z* | r.i.[c] | *m/z* | r.i.[c] |
| $[Eu(TPP)(Pc)]^+$ | 1277.3 | 1277.3 | 92.8 | 1277.2 | 69.3 | 1277.2 | 36.5 |
| $[Eu(TPP)(Pc)]^{2+}$ | 638.7 | 638.6 | 0.6 | 638.6 | 1.1 | — | — |
| $[Eu(TPP)(Pc)]^{3+}$ | 425.8 | 425.9 | 4.7 | 425.9 | 2.2 | — | — |
| $[Eu(TPP)(Pc)]^{5+}$ | 255.5 | 255.6 | 0.5 | 255.5 | 0.2 | — | — |
| $[Eu(TPP)]^+$ | 765.1 | — | — | — | — | 765.1 | 100.0 |
| $[Eu(TPP)]^{3+}$ | 255.1 | — | — | 255.1 | 1.4 | — | — |
| $[Eu(Pc)]^+$ | 665.1 | — | — | 665.1 | 12.1 | 665.1 | 11.9 |
| $[Eu(Pc)]^{3+}$ | 221.7 | — | — | 221.7 | 0.6 | — | — |

[a] Ionic species observed under non-CID conditions are listed for comparison.
[b] Mass corresponding to the most abundant isotopic peak.
[c] r.i. denotes relative intensity.

configuration of the heteroleptic triple-decker complexes. Depending on the nature of the ligands, it is concluded that both symmetric and asymmetric complexes can be formed. In the europium systems, $Eu_2(TPP)(Pc)_2$ and $Eu_2(TPP)_2(Pc)$, the former takes the asymmetric configuration as (TPP)Eu(Pc)Eu(Pc), whereas the latter adopts the symmetric configuration as (TPP)Eu(Pc)Eu(TPP). Second, there is evidence to suggest that charge-transfer processes occurred prior to molecular fragmentation under CID conditions. The tandem mass spectra of the europium complexes showed the occurrence of some unexpected fragment ions under both NS dissociation and SORI-CID conditions. The formation of these fragment ions can be explained by using a mechanism involving charge transfer. Based on the comparison of the fragmentation patterns observed in double- and triple-decker complexes, it is concluded that intramolecular charge-transfer processes were more likely to occur than intermolecular processes under the present experimental conditions.

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